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"Development of Novel Alternative Technologies for Decontamination of Warfare Agents: Electric Heating with Intrinsically Conductive Polymers"

Submitted by

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PREFACE

This is the final technical report on a project sponsored by US Army Research Office under Research Agreement No. DAAD19-02-1-0325. The report has been resulted from a collaborative research work between Drexel University and US Army Edgewood Chemical Biological Center. The Drexel University team includes Dr. Yen Wei, Principal Investigator on this project, Dr. Shuxi Li and Miss Elizabeth Wei. The US Army team includes Mr. Brian MacIver. As a collaborator, Dr. Alexander Grabowski of German Ministry of Defense has also made significant contributions to this project. The project has been monitored by Dr. Stephen Lee of ARO. We are most grateful to Dr. Lee for his advices, assistance and support.

SECTION I. Summary

So far, all the systems developed for detoxification and decontamination of chemical and biological weapons have been based on the use of chemical or biological agents. Here, we present a novel, simple, non-chemical/biological, multipurpose, re-useable, low-cost, alternative technology for decontamination based on electric (i.e., Ohmic or Joule)-heating with conducting polymers. The basic concept is that electrically conducting polymers, such as polyaniline, can be used as coatings or fabrics on military equipment (e.g., tanks, personnel carriers, artillery pieces, etc.) and installations (e.g., buildings and other structures); and that these conducting polymers function as heating elements to convert applied electric energy to thermal energy, which would raise the surface temperature of the coatings and fabrics high enough to thermally decompose the chemical or biological warfare agents on the equipment or installations. In this report, we have demonstrated this concept by employing conducting polyaniline as both coatings and electric heating element on steel panels that were pre-coated with electrically insulating polyurethane. Through embedded metallic (e.g., copper) wire or carbon fiber electrodes, household alternating current can be applied to the polyaniline-coated panels, leading to a rapid increase in the surface temperature to 120-180°C within a few minutes. The system is very easy to fabricate, re-usable and can undergo several heating-cooling cycles without significant damage. Since many chemical (e.g., HD and G-type agents) and biological (e.g., bacteria, viruses, toxins and spores) warfare agents would be decomposed or detoxified at elevated temperatures (e.g., 120-180 °C), this novel technology is multipurpose for decontamination of military equipment and installations. Furthermore, the use of conducting polymers for electric heating is, to the best of our knowledge, a novel application of conducting polymers and has not been reported in the literature.

SECTION II. Detailed Results, Discussion and Experimental Methods

I. Introduction

Attributed to the "evil doing" of a great chemist, Dr. Fritz Haber (1918 Nobel Laureate in Chemistry for his discovery of ammonia synthesis), chlorine gas was first used as chemical warfare agent on April 1915 in the second battle of Ypres during the World War I. Since then, chemical and biological warfare agents have been a lethal weapon system in the arsenals of many countries. In the post-cold war era or more contemporarily speaking, in the war against terrorism, the threats of warfare agents, such as 2,2'-dichlorodiethyl sulfide (HD or mustard gas), 3,3-dimethyl-2-butyl methylphosphono-fluoridate (GD or Soman), and numerous other chemical and biological agents from unfriendly countries and terrorist groups still exist. Demilitarization (demil) and decontamination (decon) of these weapon systems remain an important task for the modernization of the US Army. Since the WWI, various decon systems have been developed such as "German Emulsion" that uses calcium hypochlorite (high-test hypochlorite, HTH) as decontaminant. Decontamination Solution 2 (DS2), a general purpose, ready to use, non-aqueous liquid, was adopted by US armed forces in 1960, and is still in use [1]. Since then, there have been numerous efforts in developing more effective decon/demil systems [2-4] (including several by us at Drexel[3,4]). Recently, one of major developments is to employ enzymes for detoxification of warfare agents. For example, it has been demonstrated that organophosphorus acid anhydrolases (OPAA) can effectively catalyze the hydrolysis of G-type nerve agents and simulants such as difluorophosphate (DFP) [5]. However, all these decon systems explored so far are based on chemical or biological agents. Though successful to a certain extent, there are many deficiencies and formidable obstacles in the practical applications of these agents for decon and demil.

On the other hand, electrically conductive and polymers, such as polyaniline, polythiophene, polypyrrole, etc., exhibit interesting antielectrostatic, electromagnetic shielding, chemical and biological sensing, electroluminescent, electrochromic, and anti-corrosion properties[6]. A great deal of research efforts have been directed to the uses of the conducting polymers as films, coatings and paints, and as a component in nanocomposite materials. This field of research has received a highest scientific recognition recently: three pioneers of conducting polymers, A. MacDiarmid, A. Heeger and T. Shirakawa, were awarded 2000 Nobel Prize in Chemistry [6a]. One of the important features of these organic conducting polymers is that their conductivity can be controlled and fine tuned readily by changing chemical composition, oxidation state, doping level, and/or molecular weight, among others. The conductivity can be controlled in a wide range from lower than 10⁻² to greater than 10² S/cm. It should be noted that our group at Drexel has been working on various scientific and technological aspects of conducting polymers for more than 15 years [7-10].

As we proposed, the overall long-term aim of this project is to develop a novel, simple, non-chemical/biological, multipurpose, re-useable, low-cost, alternative technology for decontamination based on conducting polymers as electric-heating elements. More specifically, we proposed to apply electrically conducting polymers as fabrics and coatings on military equipment (e.g., tanks, personnel carriers, artillery pieces, etc.) and installations (e.g., buildings and other structures). The conducting polymers for this use have conductivity controlled at semiconductive level (e.g., 0.1-100 S/cm), which is higher than insulators but lower than metals. The key idea is to use conducting polymers as heating elements to convert electric energy to thermal energy that will raise the surface temperature of the fabrics and coatings high enough to thermally decompose the chemical or biological warfare agents on the equipment or installations. The electric energy could be provided from a DC or AC power supplier, including household AC current. It is noteworthy that such an application of conducting polymers has never been reported in the literature. With further research and engineering, it is highly probable that the conducting polymer fabrics could be integrated into uniforms for military or law-enforcement personnel decon applications.

II. Scope of the Work

Conductive polyaniline (PANI) has been selected for this initial study because of its low cost, good environmental stability, readily tunable conductivity, and easy synthesis and processing. Particularly, our previous research has shown that polyaniline has excellent thermal stability and exhibited reasonably good conductivity after heating at high temperatures [7,8]. In addition, polyaniline and derivatives can be prepared with controllable molecular weights, high solubility, and superior processibility [9,10]. In this work, dodecylbenzene sulfonic acid (DBSA) doped polyaniline (PANI-DBSA) was synthesized by chemical oxidative emulsion polymerization of aniline based on the literature procedures [11]. PANI-DBSA solution in toluene was used to fabricate the coatings on the steel panels that were pre-painted with the insulating polyurethane primer. A number of parallel copper wire or carbon fiber electrodes were embedded in the polyaniline coatings. Household alternating current (AC 110 V at 60 Hz) was employed as electric power source with voltage adjusted by a transformer, which was connected to the two electrodes on the conducting polymer-coated panel. By varying the applied voltage with the transformer, controlled amount of electric energy was supplied to the polyaniline coatings. The surface temperature of the polyaniline-coated panels was recorded as function of the applied voltage and time.

III. Experimental Section

III-1. Materials and Instrumentation

Aniline (Fisher) was distilled under a reduced pressure. Ammonium persulfate (Aldrich), dodecylbenzene sulfonic acid (DBSA, Acros Organics), xylene (Fisher), acetone (Fisher) tetrahydrofuran

(Fisher) and toluene (EM Science) were used as received without further purification. The steel panels that were pre-coated with insulating polyurethane primers were supplied by US Army ERDEC at Aberdeen Proving Ground, Maryland, and Fraunhofer Institute at Schmallenberg, Germany. (There should be no effect of substrate on the results in this work. The panels could be made of steel or alloys or any other metallic or nonmetallic material of specific military interest.) Commercial carbon fiber and copper wires were used as the electrodes on the polyaniline-coated panel and as conductive leads to connect the test panels to electric power source. (It should be noted that the materials for the electrodes can be wires or stripes of steel, nickel, copper, aluminum, platinum, silver, various alloys, carbon fibers, or other conductive substances.) Conductivity was measured by using either the two-probe or the four-probe techniques on the film of polyaniline and an EC&G PAR Model 173 potentiostat/galvanostat was employed as a constant current source. The resistance between the electrodes across the coating layer was measured by using a Digital Multimeter (Waveter 5XL). The temperature on the surface of the coating layer was measured with a digital Thermocouple Thermometer having a flat-head measuring probe (Paul N. Gardner Co., Inc.). The thickness of coatings was measured with a digital micrometer screw gauge (Mitutoyo Co. Japan). A jug mill (U.S. Stoneware) was used to aid the preparation of the PANI-DBSA solution.

III-2. Polymerization

Polyaniline-DBSA powder was synthesized by chemical oxidative emulsion polymerization based on the procedure described by Osterholm et al.[11] As a typical procedure, a solution of 9.32 g (0.100 mol) of aniline, 48.33 g (0.150 mol) of DBSA, 127 g of xylene and 300 mL of distilled water were mixed in a 1-L Erlenmeyer flask at room temperature. After the DBSA was dissolved completely under vigorous stirring, a milky emulsion was formed. The emulsion was cooled to about 0-5°C in an ice bath. Polymerization was initiated by dropwise addition of 22.83 g (0.100 mol) ammonium persulfate in 200 mL distilled water over 1.5 h with vigorous stirring. After polymerization for 24 h, the viscous emulsion was poured into 800 mL acetone to precipitate the PANI-DBSA complex. The dark green powder was collected on a Buchner funnel and was washed three times with 150 mL acetone, three times with 150 mL distilled water, and another three times with 150 mL acetone. Finally, the product was dried in a vacuum oven for 48 h at 35 °C.

III-3. Preparing of PANI-DBSA-toluene solution

The ratio of DBSA to aniline unit (i.e., PhN) in PANI should be approximately 1.0 in order to render PANI-DBSA complex soluble in a non-polar solvent [12]. Hence, a mixture of 3.620 g (0.040 mol PhN) PANI-DBSA, 9.660 g (0.030 mol) DBSA and 190 mL toluene was ground in a jug mill for 20 h at room temperature to afford a 7.5wt % PANI-DBSA solution in toluene.

III-4 Coating the panels and installing the electric probes

Two sets of steel panels with insulating polymer coatings, (1) 10 x 10 x 0.058 cm and (2) 10 x 35.5 x 0.175 cm, were employed as substrates. The 7.5wt % PANI-DBSA-toluene solution was poured on the surface of the panel and covered the whole surface uniformly with a bar coating facility. After drying by flowing air through, the PANI-coated panel was dried for 24 h again in an oven at 80-90 °C. The copper electric wires (D=0.159 mm, 8 filaments) or the carbon fibers were embedded, parallel to each other, in the PANI coatings as the electrodes. The adhesion of the electrodes to the PANI coatings was further ensured by applying a small amount of PANI-DBSA-toluene solution around the electrode embedment. The length of the electrode in contact with polyaniline coating on the panel was 9-10 cm. The distance between two parallel-embedded electrodes was 9 cm unless otherwise specified. After drying the newly

applied PANI-DBSA adhesive in flowing air and at 80-90 °C for 24 h, the panels with PANI coating and copper or carbon fiber electrodes/leads were ready for electric heating tests.

III-5. Application of alternating current on the PANI-DBSA coating layer

Conventional household alternating current (AC 110 V at 60 Hz) was applied on the PANI-coatings through a transformer. Thus, the AC source was connected to a lab transformer. Two electric wires were connected between the transformer and two electrodes embedded in the coating layer. A digital multimeter was connected in parallel with the transformer to measure the voltage applied between the electrodes. The surface temperature of the coatings was measured at the center of the panel with a flatheaded digital thermometer.

IV. Results and discussion

IV-1. The relationship between the distance of the electrodes and electric resistance

The copper electrodes were adhered on the PANI-DBSA coating layer at several positions, marked as A, B, C and D with various inter-electrode distances. The electric resistance between two electrodes was measured using direct current source and data are summarized in Table 1. As anticipated from Ohm's law, the resistance was found to be directly proportional to the distance between the electrodes. Such resistance values, typical for DBSA-doped polyaniline [12], will be used directly as the indications of conductivity level of the coatings because it is difficult to measure the conductivity precisely in this two-electrode-embedded coating configuration.

Table 1. The relationship between the distance of two probes and electric resistance.

| Distance (cm) | A | 8.5 | В | В | 9.5 | С | С | 9.5 | D |
|-----------------------|---|-----|----|---|-----|----|---|-----|---|
| Electric | Α | 13 | В | В | 14 | С | C | 15 | D |
| Resistance (Ω) | Α | | 25 | С | | | | | |
| | | | | В | | 27 | D | | |
| | Α | | | | 38 | | | | D |

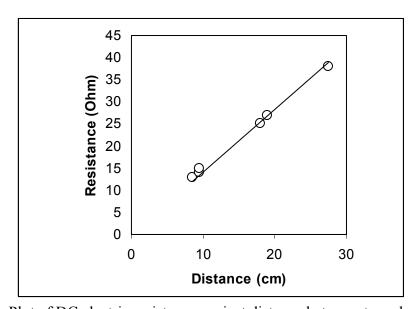


Fig. 1. Plot of DC electric resistance against distance between two electrodes.

IV-2. Electrothermal effect (electric, ohmic or joule heating) by polyaniline

IV-2a. The copper wires as electrodes

We measured the surface temperature of PANI-coated panels at various time intervals at different applied voltages and data for 4 representative samples are summarized in Table 2. In Samples 1 and 2, the applied voltage was fixed at 50 and 45 volts. Voltage was varied for Samples 3 and 4. Comparing Samples 1 and 3 up to 3 minutes, the surface temperature of Sample 1 rapidly increased to 140 °C while that of Sample 3 increased to 100 °C. This could be attributed to the low initial resistance of Sample 1. At lower applied voltage (e.g., 45 volts for Sample 2), the rate of the temperature increase was lower (e.g., 90°C at 3 min). On the other hand, higher voltage (e.g., 54-58 volts for Sample 4) resulted in higher rate of temperature increase (e.g., 147 °C at 3 min). The relationship between the surface temperature of the panel and the time period upon applying voltage in the four samples is also shown in Figure 2. In general, the surface temperature for all samples increased to a plateau values within 1-3 min. After that, there was no further significant change in temperature. This could be attributed to the heat dissipation from the polymer surface to ambient. The rate of heat generation and dissipation might have reached an equilibrium after a few minutes in these systems. The reason for changing the applied voltage in Samples 3 and 4 was to reach and maintain a surface temperature by adjusting the power output. It is foreseeable that with a data feed back mechanism, the future design will enable a programmable heating process with desired heating rate and plateau temperature at which decontamination of targeted chemical and biological warfare agents can be achieved. Since there are many complicated factors that affect the electric-tothermal energy conversion and heat transfer dissipation, it may not be meaningful to carry out further quantitative analysis of these data at this time.

Table 2. The relationship between surface temperature, time and voltage in the polyaniline-coated panels with copper wire as electrodes.

| | Sample 1 Samp | | Samp | le 2 | Sample 3 | | Sample 4 | |
|-----------------------|---------------|------|-------|------|----------|------|----------|------|
| Initial | 16.0 | | 52.7 | 52.7 | | 60.0 | | |
| Resistance (Ω) | | | | | | | | |
| Thickness (mm) | 0.018 | 3 | 0.033 | | 0.035 | | 0.023 | 8 |
| Time (min) | T °C | Volt | T °C | Volt | T °C | Volt | T °C | Volt |
| 0 | 23.2 | 0 | 23.2 | 0 | 23.2 | 0 | 23.2 | 0 |
| 0.5 | 72.1 | 50 | 40.9 | 45.2 | 75.8 | 50.0 | 94.3 | 58.6 |
| 1 | 124.3 | 50 | 54.8 | 45.3 | 91.6 | 50.2 | 120.3 | 58.5 |
| 1.5 | 134.2 | 50 | 71.2 | 45.3 | 99.3 | 50.2 | 132.0 | 58.0 |
| 2 | 130.8 | 50 | 80.3 | 45.0 | 94.0 | 50.2 | 136.2 | 55.1 |
| 2.5 | 134.5 | 50 | 87.1 | 45.4 | | | 141.4 | 53.9 |
| 3 | 140.0 | 50 | 90.3 | 45.4 | 100.1 | 50.2 | 147.3 | 54.1 |
| 4 | | | 95.1 | 45.4 | | | 153.9 | 54.4 |
| 5 | | | 95.2 | 45.5 | 102.5 | 55.3 | 144.4 | 54.2 |
| 6 | | | | | 110.5 | 55.4 | 148.4 | 54.1 |
| 7 | | | | | | | 147.0 | 45.4 |
| 8 | | | | | | | 139.7 | 41.1 |
| 10 | | | | | 116.0 | 61.2 | | |
| 14 | | | | | 118.4 | 61.1 | | |
| Resistance (Ω) | 111.0 | | 74.6 | | 115.0 | | 81.4 | |
| after cooling | | | | | | | | |

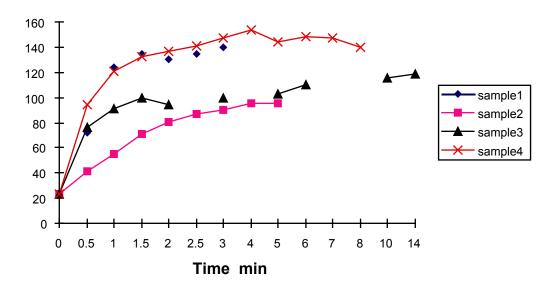


Fig. 2. The relationship between the surface temperature (y axis in °C) and time (x axis in min).

After the surface temperatures of the panels reached the plateau values, the power source was turned off and the system was allowed to cool down to room temperature. As noted in Table 2, the resistance of the samples generally increased after such a heating-cooling cycle. There are several possible reasons that could account for the increase in resistance, including thermal degradation of polyaniline, electrochemical overoxidation, and/or loss of dopant molecules [7]. To test the re-usability of the system, the panels were subjected to repeated heating-cooling cycles under various applied voltages. Some typical results are summarized in Table 3 and plotted in Figure 3. Again, at low applied voltage (e.g., 20 volts in the 1st cycle), the system was heated up slowly. At high applied voltages (e.g., 45-56 volts in the 2nd, 3rd and 4th cycles), the surface temperature of the panel rapidly increased to 110-120 °C within 3 min.

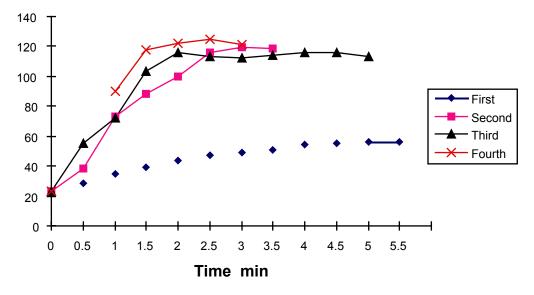


Fig. 3. The relationship between the surface temperature (y axis in °C) and time (x axis in min) with repeated 4 heating-cooling cycles.

Table 3. The relationship between temperature, voltage and time when the sample was tested repeatedly for 4 heating-cooling cycles. The thickness of the coating: 0.030 mm.

| | First | | Second | | Third | | Fourth | | |
|------------------------|-------|------|--------|------|-------|------|--------|------|--|
| Initial | 62 | | 6.5 | 65.9 | | 78.9 | | 80.8 | |
| Resistance(Ω) | | | | | | | | | |
| Time (min) | T °C | Volt | T °C | Volt | T °C | Volt | T °C | Volt | |
| 0 | 23.2 | 0 | 23.2 | 0 | 23.2 | 0 | 23.2 | 0 | |
| 0.5 | 28.8 | 20.1 | 38.2 | 44.8 | 55.0 | 52.5 | | | |
| 1 | 34.6 | 20.1 | 73.4 | 44.7 | 72.6 | 51.9 | 89.9 | 56.4 | |
| 1.5 | 39.1 | 20.1 | 88.1 | 44.8 | 103.5 | 51.5 | 117.8 | 53.3 | |
| 2 | 43.9 | 20.1 | 99.9 | 44,9 | 115.8 | 52.3 | 122.3 | 53.9 | |
| 2.5 | 47.7 | 20.1 | 115.6 | 45.0 | 113.1 | 39.7 | 124.5 | 53.9 | |
| 3 | 49.0 | 20.1 | 119.3 | 45.0 | 112.0 | 39.4 | 121.5 | 52.6 | |
| 3.5 | 51.2 | 20.1 | 118.9 | 45.0 | 113.9 | 39.0 | | | |
| 4 | 54.0 | 20.1 | | | 115.9 | 39.2 | | | |
| 4.5 | 55.2 | 20.1 | | | 116.1 | 39.2 | | | |
| 5 | 56.2 | 20.1 | | | 113.0 | 37.9 | | | |
| 5.5 | 56.6 | 20.1 | | | | | | | |
| Resistance after | 65.9 | | 78.9 | | 80.8 | | | | |
| cooling (Ω) | | | | | | | | | |

It should be noted that after several heating-cooling cycles the quality of the polyaniline coating remained good and the initial resistance only increased marginally (e.g., from 62 to 81 Ohms). These results, even though far from possible optimal, suggest that the polyaniline coating systems may have the stability good enough to be used repeatedly in the decontamination applications for multiple times.

IV-2b. The carbon fibers as the electrodes

When the copper wires were used as the electrode material, if the applied voltage was over 60 volts, electric sparks were often observed at the interface between the copper wires and the polyaniline coatings on the panels. Generation of such sparks at high voltages could be caused by the very large difference in conductivity between copper ($\sim 10^5$ S/cm) and polyaniline ($\sim 10^{-1}$ -10 S/cm)[6a]. If one wishes to apply high voltages to achieve high temperature rapidly, copper electrodes would not be the material of choice. Therefore, we tested carbon fibers as electrodes because they have much lower conductivity ($\sim 10^2$ - 10^3 S/cm) than copper. All the experimental designs were kept the same as those described in above section except the carbon fibers instead of copper wires were used as the electrodes embedded in polyaniline coatings. The surface temperatures of PANI-coated panels at various time intervals at different applied voltages for 4 representative samples are summarized in Table 4. There are several general trends that are similar to those observed for copper electrodes. First, the coatings with lower initial resistance showed higher rate of surface temperature increase (Sample 1). Second, higher applied voltages resulted in fast increase in the surface temperature.

However, there are several remarkable improvements with the use of carbon fibers over that of copper wires as electrodes. First, high voltages of >60 volts can be applied without electric sparks. This enables the system to achieve high surface temperature rapidly. As shown in Figure 4, the surface temperature of 130-150°C was achieved within 2 min. It should be noted that because of the expanded range of applied voltage, the surface of the coatings can be heated to 130-150 °C rapidly *regardless* of the initial resistance of the coatings. The sample with initial resistance of 231 Ohms reached 140°C in 2 min by applying a high voltage of 91 volts. This is of great practical importance because it significantly

increases the tolerance of materials for this new technology. That is, a desired temperature can be achieved in a desired short time period by changing applied voltage for polyaniline coatings that may have very different conductivities. Furthermore, carbon fibers appear to have better compatibility with polyaniline so that the adhesion of the electrodes to polyaniline coatings was enhanced. Finally, carbon fibers are lighter and generally less expansive than many metallic electrodes including copper.

Table 4. The relationship between surface temperature, time and voltage in the

polyaniline-coated panels with carbon fibers as electrodes.

| | Samj | ple 1 | Sample 2c | | Sample 3c | | Sample 4c | |
|--------------------|-------|-------|-----------|------|-----------|------|-----------|------|
| Initial Resistance | 23.5 | | 43.3 | | 114.0 | | 231.0 | |
| (Ω) | | | | | | | | |
| Thickness (mm) | 0.1 | 11 | 0.112 | | 0.098 | | 0.040 | |
| Time (min) | T °C | Volt | T °C | Volt | T °C | Volt | T °C | Volt |
| 0 | 23.4 | 0 | 23.2 | 0 | 23.2 | 0 | 23.2 | 0 |
| 0.5 | 121.3 | 41.9 | 99.1 | 58.0 | 104.4 | 81.5 | | |
| 1 | 143.6 | 42.0 | 124.1 | 58.8 | 132.6 | 81.4 | 107.0 | 90.9 |
| 2 | 153.1 | 42.0 | 133.6 | 58.9 | 147.0 | 81.6 | 140.0 | 91.1 |
| 3 | 148.8 | 42.4 | 138.1 | 58.8 | 148.6 | 81.9 | 145.7 | 91.3 |
| 4 | 145.0 | 42.5 | 139.6 | 59.0 | 147.5 | 81.7 | 150.2 | 91.3 |
| 5 | 149.1 | 42.5 | 142.6 | 64.2 | 150.2 | 81.6 | 148.9 | 91.2 |
| 6 | 147.9 | 42.5 | 145.9 | 64.5 | 147.8 | 81.8 | 150.9 | 91.2 |
| 7 | | | 146.0 | 64.3 | | | | |
| 8 | | | 139.5 | 66.0 | | | | |
| 9 | | | 142.4 | 66.0 | | | | |
| 10 | 135.2 | 42.5 | | | 135.5 | 81.8 | 142.1 | 91.2 |
| 15 | | | | | 130.1 | 81.9 | 135.7 | 91.5 |
| Resistance after | 140.4 | | 160.0 | | 303.0 | | 374.0 | |
| cooling (Ω) | | | | | | | | |

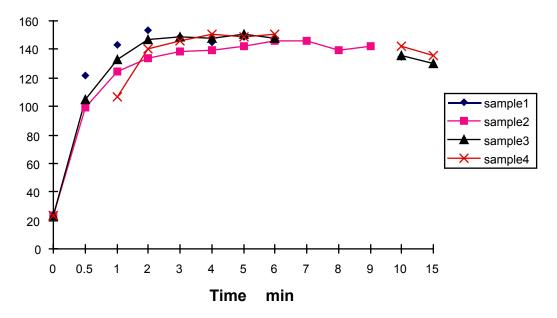


Fig. 4. Plot of the surface temperature (y axis in °C) against time (x axis in min) for the samples with carbon fiber electrodes.

The end of electric heating, the power source was turned off and the system was cooled to room temperature. The resistance of the samples, again, generally increased after the heating-cooling cycle similar to the cases with copper wire electrodes. To test the re-usability of the coatings, two heatingcooling cycles were performed on a sample with carbon fiber electrodes. As shown in Table 5 and Figure 5, an increase in the surface temperature to 140-160 °C within 2-3 min was readily achievable. These data also demonstrate that polyaniline coatings were remarkably stable even after the electric heating at about 150-180 °C for more than 10 min in two cycles.

Table 5. The relationship between temperature, volts and time when the sample was tested repeatedly. The thickness of coating: 0.207 mm

| repeatedry. The tr | iickiicss of coatilig | 5. 0.207 Hill. | | |
|-----------------------|-----------------------|----------------|-------|------|
| | Fi | rst | Sec | ond |
| Initial | 23 | 3.0 | 70 | 8.8 |
| Resistance (Ω) | | | | |
| Time (min) | T °C | Volt | T °C | Volt |
| 0 | 23.2 | 0 | 23.2 | 0 |
| 0.5 | 106.6 | 50.7 | 106.6 | 61.3 |
| 1 | 116.1 | 51.0 | 145.7 | 61.3 |
| 1.5 | 125.1 | 50.9 | 166.4 | 61.3 |
| 2 | 130.5 | 50.8 | 166.0 | 55.3 |
| 2.5 | 138.8 | 50.7 | 168.1 | 55.3 |
| 3 | 143.3 | 50.6 | 164.0 | 55.3 |
| 3.5 | 157.6 | 50.0 | 164.6 | 54.8 |
| 4 | 168.1 | 50.3 | 164.5 | 55.2 |
| 5 | 180.6 | 50.3 | 164.8 | 55.4 |
| 6 | 184.1 | 50.3 | 164.2 | 55.4 |
| 7 | 187.3 | 50.5 | | |
| 8 | 175.4 | 50.7 | 162.4 | 55.3 |
| 9 | 174.1 | 50.7 | | |
| Resistance (Ω) | 70 | 0.8 | 10: | 5.8 |
| after cooling | | | | |

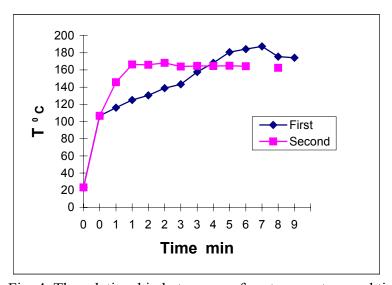


Fig. 4. The relationship between surface temperature and time with repeated heating-cooling cycles.

If the desired surface temperature of the panel is 140-150 °C, from above data with the carbon fibers as electrodes, the applied voltage can be estimated based on the initial resistance of the polyaniline coatings as shown in Figure 5. Such an empirical relationship could guide the experiment design.

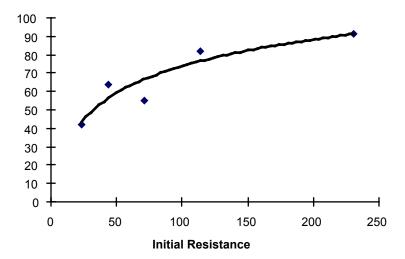


Fig. 5. To reach 140-150 °C within 2-3 min, an approximate relationship between the initial resistance (x axis in ohm) and the voltage to be applied (y axis in volt)

V. Conclusions and Further Research Designs

We have demonstrated that conducting polymers such as polyaniline can be employed as coatings and electric heating element on metallic substrates or panels pre-coated with electrically insulating polymers. Through embedded metallic (e.g., copper) wire or carbon fiber electrodes, household alternating current can be applied to the polyaniline-coated panels leading to a rapid increase in the surface temperature to 120-180°C within a few minutes. The system can undergo several heating-cooling cycles without significant damage. Since many chemical and biological warfare agents would be decomposed or detoxified at elevated temperatures (e.g., 120-180 °C), this novel application of conducting polymers represents a new, non-chemical/biological, multipurpose, re-useable, low-cost, alternative technology for decontamination of military equipment and installations. The feasibility of such a new technology has been firmly established from this work with the following specific conclusions:

- (1) Polyaniline (PANI) can be used repeatedly as an electric heating material that converts electric energy to thermal energy, leading to a temperature increase to 120-180 °C within a few minutes upon applying household 60 Hz AC at 40-90 volts through a transformer.
- (2) For the practical application, the self-doped PANI-DBSA and low-toxic solution of PANI-DBSA-toluene could be readily used to fabricate the polymer coatings.
- (3) The copper wires and carbon fibers can be embedded in the polyaniline coatings as the electrodes and as electric leads upon which the voltage is applied.
- (4) The carbon fibers are much better electrode materials than the copper wires. The interface between carbon fiber electrode and polyaniline coating can endure higher voltage (e.g., 60-90 volts) of alternating current in comparison with that between copper wires and polyaniline.

To fully develop this novel alternative decontamination technology for practical military applications, we have designed many further experiments. Among them, the properties of both the

conducting polymers and the electrodes should be optimized. The effects of various electric energy sources, coating formulations and electrode geometric designs on the system performance should be evaluated. In collaboration with US Army ERDEC at APG and Fraunhofer Institute at Schmallenberg, Germany, the preliminary results have shown that the system described in this work could be electrically heated up to 150 °C within 1 to 2 minutes with a great reproducibility and that at >130 °C some chemical warfare agents such as mustard gas (HD) simulant decomposed into nontoxic compounds [11]. However, further tests will be needed to evaluate the decontamination effectiveness. Besides HD, other chemical weapon systems such as G-type agents should also be tested with simulants on our new decon system. In addition, it is reasonable to expect that our system will be effective in destroy the surface-bound biological warfare agents as well because most of bio-agents such as bacteria, virus, toxins, spores, etc., are unlikely to survive the high temperatures. All the test results should be utilized as feedback to further improve the synthesis and processing of the polymers, the coating formulations and the coating fabrication procedures for maximum performance in converting electric energy to thermal energy for the decon applications. Other conductive materials, such as polythiophenes, polypyrroles, carbon-containing or metal-containing blends/composites, etc., can also be produced and evaluated as the electrothermal component for the alternative decon application. To further improve the adhesion of conducting polymer coatings with metallic or non-metallic substrates, conducting polymer-inorganic hybrid materials can be employed [14]. Since the conducting polymers can also be coated onto conventional textiles or span into fibers, the same technology is extendable to making decon fabrics and clothing for personnel, equipment and installation decontamination. It should also be noted that electrically conducting and/or electroactive polymers have many interesting electrooptical properties and their applications as antielectrostatic, electromagnetic shielding, chemical and biological sensing, electro-voltaic electroluminescent, electrochromic, battery, and anti-corrosion materials have been explored. Therefore, we can envision that a new integrated multifunctional system could be developed based on the conducting polymers for not only decontamination but also numerous other applications.

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